

JUNE 22, 1992

**USERS SCRAMBLE TO MEET
1996 PHASEOUT DEADLINE
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NEWS OF THE WEEK

■ The Earth Summit in Rio de Janeiro ended with hope raised by progress in several areas but disappointment over failures in other areas. **Page 4**

■ The U.S. House of Representatives votes to kill the Superconducting Super Collider, causing concern about whether science and technology will be hit further as budget pressures build. **Page 5**

■ Launch of NASA's space shuttle *Columbia* later this week will initiate a series of Microgravity Laboratory missions to examine the effects of low gravity on crystal growth, fluid dynamics, and other processes. **Page 5**

■ June 30 has been set for the split of Union Carbide into two separate companies, but a lawsuit threatens to scuttle the plan. **Page 5**

■ NIH researcher Robert C. Gallo will speak this week about the controversy surrounding his lab's role in the 1984 discovery of the AIDS virus. **Page 6**

■ A power shortage on NASA's Upper Atmosphere Research Satellite has shut down most instruments gathering data on the ozone layer. **Page 6**

COVER: Du Pont visiting researcher checks thermocouples on a freezer-evaporator in tests using chlorofluorocarbon substitutes carried out at Oak Ridge National Laboratory. Photo by Tom Cerniglio

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BUSINESS

Japan's chemical industry hasn't enjoyed success of other high-tech areas despite visionary efforts. **Page 15**

Dow Chemical has launched \$1 million program to promote plastics recycling. **Page 16**

GOVERNMENT

Reduction of waste generated at chemical plants yields environmental and economic benefits. **Page 18**

Bill would add severe criminal penalties to environmental regulations in effort to force companies to speed up their efforts to stop polluting. **Page 20**

SCIENCE/TECHNOLOGY

Research results show that ribosomal RNA is probably sufficient for peptide bond formation and that ribozyme catalyzes hydrolysis of aminoacyl esters. **Page 22**

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Exhibits at ACHEMASIA meeting in Beijing featured basic equipment and control systems; presentations emphasized energy problems and biochemical production. **Page 25**

BOOKS

"The Human Blueprint," by Robert Shapiro, explores how the human genome project became a major federally funded research undertaking. **Page 28**

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NEWS FOCUS



Pending ban on chlorofluorocarbons has industry and consumers alike preparing to use CFC alternatives in products ranging from refrigerators to metered-dose drug dispensers. **Page 7**

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LETTERS

CHEMICAL SAFETY

Incomplete photocatalytic oxidation of TCE

There has been recent interest and publicity regarding the use of UV-irradiated TiO_2 as a photocatalyst to destroy chlorinated chemicals in air. Publications have appeared regarding the destruction of trichloroethylene (TCE), a widely occurring contaminant in water and soils. Such experiments are easy to carry out in the laboratory at room temperature, using ordinary black-light fluorescent lamps and simple reactors with supported TiO_2 .

This letter is to warn experimenters that the incomplete photocatalytic oxidation of TCE, perchloroethylene, and perhaps other chlorinated hydrocarbons in the gas phase over TiO_2 can yield considerable quantities of phosgene and chlorine. The phosgene has been unambiguously identified in three different reactors at the National Renewable Energy Laboratory using direct mass spectrometry and on-line Fourier transform infrared spectroscopy.

From initial TCE concentrations of 100 ppm (volume) in moist or dry air, phosgene concentrations up to about 75 ppmv were seen at 98% TCE destruction (chlorine concentrations were comparable). This is well above the threshold limit value of 0.1 ppmv. In initial studies by others using gas chromatographic (GC) analysis [see, for example, *Environ. Sci. Technol.*, **26**, 492 (1992)], phosgene and chlorine have not been reported, perhaps because of the sample collection procedures or the GC columns used. We are raising a laboratory safety issue and not passing judgment on the ultimate potential of the technology, since process solutions exist to prevent formation of, or to remove, such by-products.

Tom Milne
Mark Nimlos

Chemical Technologies Research Branch
National Renewable Energy Laboratory
Golden, Colo.

MSDS database

Janice Long (C&EN, May 18, page 7) has provided a comprehensive, timely description of the proposed standard for the preparation of material safety data sheets (MSDSs). The standard is an impressive accomplishment of the Chemical Manufacturers Association and its MSDS work group. The benefits of the standard for health and safety and for international trade will likely far outweigh the sizable costs of implementing the standard.

The article closes with the comment that many chemical users have asked for a centralized source of MSDSs. One centralized source of MSDSs already exists and is widely available at reasonable cost. This is the MSDS database produced by the Canadian Centre for Occupational Health & Safety (CCOHS).

During the past 10 years, CCOHS has worked in consultation with chemical producers and users to build a database containing over 80,000 MSDSs from over 470 North American chemical suppliers. The database reproduces the complete texts and formats of MSDSs exactly as

they are provided by chemical suppliers. Most MSDSs are submitted in electronic form as text files, following simple specifications. MSDS collections are updated simply by providing a new text file with new content and/or format.

The MSDS database is available throughout the world on-line on STN International as "MSDS-CCOHS." It is also available on CD-ROM from CCOHS. In these forms, it has over 2500 users in about 40 countries.

As yet, the MSDS database contains only a fraction of all existing MSDSs, but it continues to grow as suppliers and users recognize its value in helping to comply with occupational, environmental, and right-to-know requirements.

The database is produced and distributed at moderate cost because of the voluntary participation and excellent cooperation of suppliers. Administrative overhead is low, and most of the subscription income is used to process new collections and updates.

Robert Whiting

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Industry, Consumers Prepare for Compliance with Pending CFC Ban

Everything from refrigerators to metered-dose drug dispensers will likely be affected by move from chlorofluorocarbons to alternatives

Pamela S. Zurer, C&EN Washington

For chlorofluorocarbons (CFCs), doomsday is now only three and one half years away. Last February, President Bush—prompted by new evidence of the continuing deterioration of the stratospheric ozone layer—unilaterally moved the deadline for the U.S. to cease production of CFCs and other ozone-depleting chemicals from the year 2000 to the end of 1995.

For the myriad industries, businesses, and consumers that have relied on CFCs, the ramifications of the coming demise of the chemicals vary. Some have already identified substitute chemicals, processes, and technologies, and have eliminated all CFC use. Others are well on their way. Some are poised to take the plunge once questions about the safety and environmental acceptability of certain substitutes are cleared up and their relative price goes down.

However, still other CFC users, most notably manufacturers of household refrigerators, were already struggling to meet the previous phaseout deadline of 2000. The loss of four years in which to engineer and test replacements has them anxious and worried.

Complicating matters further, some hydrochlorofluorocarbons (HCFCs) that are being substituted for CFCs will themselves be phased out early in the next century. Rapid replacement of CFCs with HCFCs and hydrofluorocarbons (HFCs) is necessary to achieve an early phaseout of CFCs, according to United Nations-sponsored assessments. But HCFCs carry some chlorine into the stratosphere, although they are less damaging to the ozone layer than fully halogenated compounds. That means they face a ban sooner or later, and certain industry sectors must look for a second set of alternatives, this time for the HCFCs.

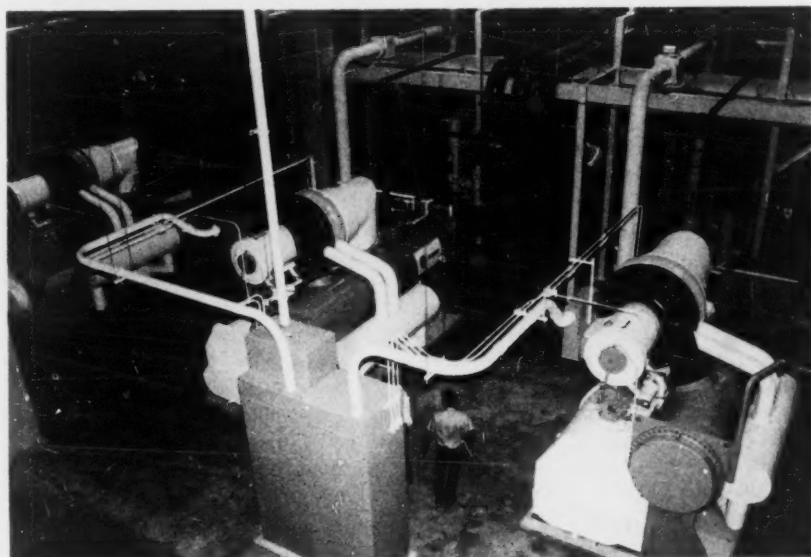
The brief history of CFC regulation is a tale of policymakers struggling to keep up with a stream of bad news about the stratospheric ozone layer, which blocks most damaging solar ultraviolet radiation from reaching Earth's surface. When the negotiations that eventually led to the Mont-

real Protocol on Substances That Deplete the Ozone Layer began in the mid-1980s, the atmospheric science community believed controlling the growth in production of CFCs and halons (fluorocarbons that contain bromine) would be enough to ward off significant ozone destruction.

Thus, the original terms of the treaty, agreed to in 1987, called for a cutback in CFC production to 50% of 1986 levels by 1998. The output of halons was to be frozen at 1986 levels in 1992.

But the treaty was out of date well before it went into effect in 1989. By then, scientists had confirmed that chlorine and bromine from CFCs and halons are the cause of the recurring dramatic seasonal losses of ozone at the South Pole known as the Antarctic ozone hole (C&EN, May 30, 1988, page 16). Moreover, a careful evaluation of measurements taken from Earth and from satellites had revealed a small but ominous erosion of the ozone layer all over the globe (C&EN, March 21, 1988, page 6). And research in the Arctic found the stratosphere there chillingly similar to the Antarctic's, with only the milder northern winters thus far preventing significant ozone depletion (C&EN, March 6, 1989, page 29).

Those findings led the international community to



These chillers for air-conditioning large buildings use HCFC-123 in place of CFC-11

strengthen the Montreal protocol. Its 1990 London amendments require complete phaseout of CFCs, halons, and carbon tetrachloride by the end of the century. Methyl chloroform (CH_3CCl_3) is to be banned by 2005.

In the U.S., the 1990 Clean Air Act imposed similar controls, although its deadline for a methyl chloroform phaseout is 2002. The U.S. law differs significantly from the international treaty, however, in how it treats HCFCs. The London amendments call for voluntary phaseouts of "transitional substances" (HCFCs) no later than 2040, whereas the Clean Air Act forbids production of HCFCs after 2015 except for servicing existing equipment and imposes a total ban after 2030.

The Clean Air Act also requires U.S. officials to speed up the phaseouts if necessary to protect human health and the environment. It was under that authority that President Bush in February ordered the end of CFCs, halons, carbon tetrachloride, and methyl chloroform production four years earlier than planned (C&EN, Feb. 17, page 5). He also called for a review of HCFCs and of methyl bromide, recently identified as a major source of bromine in the stratosphere.

Bush acted after the National Aeronautics & Space Administration announced in February that global ozone erosion was occurring faster and extending farther than previously believed. Scientists taking part in NASA's second airborne research expedition over the Arctic also concluded there is a high likelihood of an ozone hole developing in the Northern Hemisphere during the next 10 years (C&EN, Feb. 10, page 4).

Their findings bolstered the conclusions of last year's "Scientific Assessment of Ozone Depletion: 1991," prepared for the United Nation's Environment Program (UNEP) by an international panel of 80 scientists. That report, meant as advice to the countries that are parties to the Montreal protocol, concluded that stronger restrictions on chlorine and bromine compounds are necessary to head off even worse losses of ozone in the next decade.

So once again the Montreal protocol member nations will strengthen the treaty. When they next meet in Copenhagen in November, they are expected to vote to accelerate the CFC and halon phaseout deadline to sometime in 1995 and to place as yet undetermined restrictions on HCFCs.

Making such a quick shift away from CFCs is technologically feasible, according to another 1991 UNEP study for the treaty nations. Virtually all new production—although not the use of recycled chemicals—of CFCs, halons, carbon tetrachloride, and methyl chloroform could be eliminated in industrial nations by 1995 to 1997, the report concludes.

"There are lots of good reasons to be optimistic," says Stephen O. Andersen, director of the Environmental Protection Agency's technology transfer and industry programs in the division of global change. Andersen was cochairman of UNEP's technology and economic assessment panel, which was composed of 240 members from 38 countries—the majority of whom were from industry.

"Worldwide, CFC production is already 40% below 1986 levels," he points out. "That's way ahead of the game. Progress has been faster even than what we thought was feasible when we did our last assessment in 1989."

Andersen points to several success stories that demonstrate that getting out of CFCs is proven and feasible. The assessment panel could not find a single producer of plastic



Metered-dose inhalers use CFCs to propel medication into lungs

foam food-packaging products anywhere in the world that is using CFCs, he says. In the U.S., that industry completed the switch to HCFC-22 (CHClF_2) and hydrocarbon blowing agents in early 1990, according to the Foodservice & Packaging Institute.

The panel for the first time also identified entire companies, even entire countries that have quit using CFCs. In early 1992 Northern Telecom became the first multinational corporation to halt all use of CFCs in its operations. And Sweden has remaining only one small military application for the chemicals, Andersen says.

"It's not pure proof that CFCs can be eliminated entirely," he says. "Surely Sweden could still be importing products made with CFCs. No doubt Northern Telecom still buys products made with CFCs. Nevertheless it is an incredible accomplishment."

The electronics industry as a whole has made rapid progress. It had been a heavy user of CFC-113 (CCl_3F), once the fastest growing segment of the CFC market, for cleaning printed circuit boards and other electronic components. Now, virtually all major electronics companies have pledged to eliminate CFC use by 1995, if not earlier.

To clean their products, researchers in the industry have developed aqueous and terpene-based solvents, among others. And in the quest for substitute chemicals, they also have found alternative processes and technologies—some of which are turning out to be money savers. The rewards from eliminating CFCs will become even greater during the next few years as the chemicals' prices rise as a result of shrinking supply and an increase in the taxes the U.S. imposes on them.

AT&T, for example, has patented and is marketing a "low solids fluxer," a system that entirely eliminates the need to clean electronic circuitry after soldering. The initial

cost of buying the equipment, the company claims, is recovered in less than a year.

In 1988 the electronics industry formed the Industry Cooperative for Ozone Layer Protection (ICOLP), in an effort to share advances and promote technology transfer among countries and companies. ICOLP acts as a clearinghouse for information on CFC alternatives and sponsors a database called OZONET used by companies, governments, and associations.

Such access to information will be key to getting other users of CFC-113 and methyl chloroform to give up those chemicals. Both solvents are widely used in small manufacturing and service shops for cleaning metals, for example.

"Larger users and customers have seen this on the horizon and are finding alternatives," says Ken Gedaka, a spokesman for Dow Chemical, which produces methyl chloroform. "It's harder for the smaller businesses. They don't have the capital or resources to search for substitutes or even the staff to monitor the constantly changing regulations. The mom and pop shops are nervous, indeed."

Also nervous is the American Lung Association (ALA). At its annual meeting last month, the association announced it's seeking an exemption from Bush's accelerated phaseout schedule for the CFCs in the pocket-size devices used by patients suffering from asthma, chronic bronchitis, and emphysema. ALA estimates about 25 million people in the U.S. use metered-dose inhalers, which deliver precisely measured doses of medication in aerosol form directly to the lungs. CFCs are the propellants.

The pharmaceutical industry is looking for new propellants, as well as for alternative delivery systems like dry powder inhalers. It is concentrating on two HFCs, but neither is fully compatible with all current drug formulations or device designs.

Once substitute propellants are identified, the drug companies must demonstrate to the Food & Drug Administration that they are safe and that formulations using them are effective. ALA estimates the shortest possible time needed for conversion to CFC-free inhalers is six to eight years—1998 to 2000.

In announcing the accelerated ban last February, Bush said the Administration would allow limited production of CFCs after 1995 if necessary to sustain essential uses. The White House specifically cited medical uses as a possible exemption, along with refrigeration and air-conditioning. Such exemptions are also being considered as part of the latest amendments to the Montreal protocol. In the U.S., EPA has said it will not define what essential uses will be exempt from the phaseout until 1994 at the earliest.

Another anxious group of CFC users who have asked for an exemption from the 1996 deadline are producers of home refrigerators. Besides being forced to move away from CFCs, the home appliance industry is facing stiff federal energy-efficiency require-

ments. So far, no U.S. manufacturer has switched to substitutes.

Refrigerator manufacturers use CFC-11 (CCl_3F) in the polyurethane foam insulation that fills the walls and doors of such units. The CFCs trapped within the foam contribute to its insulation value. Refrigerators also have CFC-12 (CCl_2F_2) in their compressors. Although the amounts of the chemicals per unit are small and make up only a modest part of the final cost of the product, the CFCs perform essential roles.

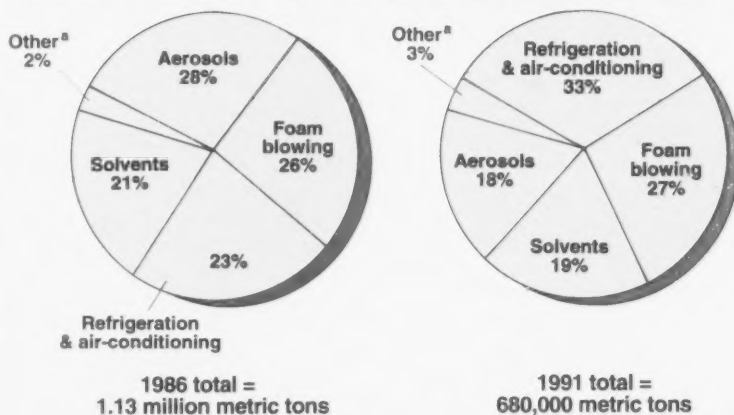
"CFCs are fundamental: They are the blood and bones of our product," says Charles Samuels, government relations counsel for the Association of Home Appliance Manufacturers (AHAM). "There's tremendous concern within the industry. We'll be the last to move out. There are significant technological and economic barriers to overcome and our members are moving with extreme caution."

Although modifications in the foaming process are allowing refrigerator manufacturers to reduce the amount of CFC-11 they've been using, they are facing major headaches getting rid of it entirely. The Appliance Research Consortium, a subsidiary of AHAM, has found that two of the most promising substitutes, HCFC-123 (CHCl_2CF_3) and HCFC-141b ($\text{CH}_2\text{CCl}_2\text{F}$), attack the plastics currently used as interior liners. They also weaken the elastomers used in items such as seals, gaskets, and O-rings.

"We've found some serious liner cracking that can't be repaired," Samuels says. "The financial consequences of liner problems developing after a few years are staggering. We make 25,000 refrigerators a day that people expect to last for 15 or 20 years with virtually no repairs. The warranty costs could be potentially disastrous."

The incompatibility problems likely can be solved by switching to different plastics and elastomers. But both HCFC-123 and HCFC-141b face additional difficulties. Last summer, despite having looked innocuous in the first rounds of toxicity tests, HCFC-123 was found to cause benign tumors in male rats (C&EN, July 22, 1991, page 21). Although it likely can be used safely in applications where

Worldwide CFC output in 1991 was 60% of 1986 level



Atmospheric chlorine levels, ozone threat will peak around turn of the century

The need for quick action on scrapping chlorofluorocarbons (CFCs) and other ozone-depleting compounds stems from their long atmospheric lifetimes. Even though their use is now being curtailed, atmospheric chlorine concentrations will continue to increase for about another 10 years because of the lag between the time CFCs are manufactured and when they reach the stratosphere. And even when their concentration begins to decrease, it will take decades for their levels to fall below those at which ozone destruction was first observed. Atmospheric scientists are very worried about what might happen in the meantime.

The situation can't get much worse over Antarctica. When the Antarctic ozone hole was first discovered in the mid-1980s, it waxed and waned from year to year. For the past several years, however, the destruction of ozone over Antarctica in the spring has been consistently deep and extensive in area, according to the 1991 scientific assessment prepared for the United Nations Environment Program.

During September and October, essentially all the ozone in the Antarctic

stratosphere is chewed up in chain reactions catalyzed by chlorine and bromine free radicals. (The ozone is eventually replenished as shifting springtime winds bring ozone-rich air from lower latitudes.) So, although the depletion there could widen geographically, it can't get more acute than it already is.

The Arctic is another story. During last winter's NASA-sponsored second Airborne Arctic Stratospheric Expedition (AASE II), scientists observed record high levels of chlorine monoxide, the free radical that is vital in key ozone-destroying reactions. The ozone-depletion cycle requires sunlight, however, and this year, an early warming in the polar regions allowed the chlorine monoxide to dissipate before the far north became strongly sunlit.

Nevertheless, a NASA satellite recorded a decrease in ozone of about 10% in certain Arctic regions last winter. "That is not an ozone hole, but it is a significant loss of ozone," Harvard chemistry professor James G. Anderson, who was chief scientist for the expedition, said this past April.

Arctic ozone depletion will most likely worsen in the coming decade. Chlorine concentrations will likely continue to increase for about 10 years and, because five out of 10 Arctic winters are colder than the winter of 1991-1992 was, during many of those years it will be cold enough, long enough for the chlorine to do serious damage.

A less acute but more pervasive loss of ozone over the rest of the globe also must be reckoned with, says Michael Kurylo, head of NASA's upper atmospheric research program. Ground and satellite observations show that winter ozone levels at northern midlatitudes decreased 6 to 8% between 1979 and 1991. Smaller but still troubling decreases have been recorded in spring and summer as far south as 30° N. Although not so dramatic as the Antarctic ozone hole or the threat of an Arctic hole, these losses are occurring over regions and in seasons where people, animals, and crops could be exposed to increased levels of damaging ultraviolet radiation.

Data from AASE II provide strong evidence that midlatitude losses are caused by chlorine- and bromine-cata-

exposures can be controlled, EPA is expected to forbid its use in foams when the agency proposes "safe alternatives" regulations later this summer.

Thus far, no such unhappy surprises have turned up in toxicity tests of HCFC-141b, which—like those on HCFC-123—are expected to be completed later this year. Use of HCFC-141b, however, is likely to be restricted because it has the highest ozone-depleting potential of any of the major CFC alternatives.

A ban on use of HCFCs-22, -141b, and -142b in new equipment by 2000 is among the demands of a coalition of three environmental groups. The Natural Resources Defense Council, Friends of the Earth, and the Environmental Defense Fund petitioned EPA last December to speed up the U.S. phaseout of ozone-depleting chemicals (C&EN, Dec. 9, 1991, page 5). They want those three HCFCs banned entirely by 2005.

EPA was supposed to have responded to the groups' petition by June 3, but missed its deadline. Eileen Claussen, director of EPA's office of atmospheric and indoor air, says the agency will include its answer to the environmental groups when it proposes regulations to implement President Bush's accelerated phaseout.

EPA's proposal will also respond to a February petition by the Alliance for Responsible CFC Policy. The alliance, a Washington, D.C.-based industry-trade group composed of CFC producers and users, countered the environmental groups' demands with its own recommendations on

HCFCs. It seeks a ban on production for new equipment in 2010, with a total phaseout by 2020.

The alliance argues that those dates would clearly signal users that HCFCs cannot be relied on as the final answer to replacing CFCs. Yet the deadlines are far enough in the future to make investment in converting to HCFCs worthwhile, while research on the next generation of substitutes continues, it says.

Rumor has it EPA is going to propose a compromise between the dates suggested by the environmental groups and the industry group, restricting HCFCs-22, -141b, and -142b use to the maintenance of existing equipment after 2005. The proposed regulations may be out within a month, though they have yet to be cleared by the Office of Management & Budget.

EPA also is supposed to publish sometime this summer a list of prohibited substitutes for particular CFC uses. Under the Clean Air Act's safe-alternatives policy, the agency must weigh both the environmental and health effects of compounds that are replacing CFCs. The rule making is complicated, Claussen says, because her staff is looking at individual chemicals and industry sectors on a case-by-case basis.

Because of its potential toxicity, for example, HCFC-123 is expected to be approved for cooling uses but not for foams or solvents. HCFC-141b, on the other hand, could be banned from solvent use because of its relatively high ozone-depleting potential.

At the pace it's moving, EPA no doubt will miss its stat-

lyzed reductions. Reactions on sulfate aerosols shift the equilibria within families of nitrogen, chlorine, and bromine species toward the active, ozone-destroying forms. And that condition will only get worse as the atmospheric halogen concentration increases during the 1990s.

"We believe we'll see about double the midlatitude loss in the next decade," says Robert T. Watson, director of NASA's process studies program office. "The international assessment of last October combined with the findings of the [AASE II] campaign clearly show the London amendments are inadequate to protect ozone in the future."

Under the London amendments—the 1990 revisions that strengthened the Montreal Protocol on Substances That Deplete the Ozone Layer—chlorine levels in the atmosphere would grow from the current 3.5 ppb to around 4.0 ppb by 2000 and then slowly decrease. Chlorine concentrations would decline to 3 ppb by about 2027 but would not go below 2 ppb, the level at which the Antarctic ozone hole first appeared, until the second half of the 21st century.



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Strengthening control measures by moving phaseout deadlines forward and making interim cuts in use can both decrease the future peak chlorine concentration and speed the rate at which the concentration declines, Watson says. Regulating hydrochlorofluorocarbons (HCFCs), which are replacing CFCs in several uses, would also help chlorine levels to decline faster.

HCFCs share many of the desirable characteristics of fully halogenated CFCs, but not their long lifetimes. The hydrogen atoms they bear make them susceptible to oxidation in the lower atmosphere, so over the long term they have a much lower potential for depleting the ozone layer.

But a portion of emitted HCFCs do enter the stratosphere and once there release chlorine atoms that destroy ozone. Although their brief lifetimes mean the atmosphere could recover quickly from large emissions of HCFCs, the short-term damage could be significant, according to a recent study by National Oceanic & Atmospheric Administration scientists Susan Solomon and Daniel L. Albritton [*Nature*, 357, 33 (1992)]. And it is in the short term—the next few decades—that danger to the ozone layer will be most acute. These scientists suggest considering restrictions on the production and use of HCFCs that have the largest short-term potential for ozone depletion.

utory deadline to finalize safe alternatives rules by Nov. 15. It has already missed deadlines for regulations regarding CFC labeling and recycling. The delays dismay not only environmental groups, but industry too.

"EPA needs to publish regulations as soon as possible," says F. Tony Vogelsberg, Du Pont's environmental manager for fluorochemicals. "We have seen reluctance in customers to switch out of CFCs. They're concerned whether the safe alternatives program will deem a particular use acceptable."

The uncertainty over how long HCFCs will be on the market is also a sticking point for current CFC users. "EPA needs to give users some clarity so they can make plans and move ahead. Owners of apartment buildings, office buildings, or grocery stores need [to believe] that you will be able to use HCFCs long enough to justify investment in conversion," Vogelsberg says.

Despite the regulatory uncertainty surrounding HCFCs, President Bush's acceleration of the CFC phaseout schedule is prompting some users to switch. For example, Trane Co. sells large centrifugal water chillers—air-conditioning units for big buildings—that can function with either CFC-11 or HCFC-123. The company has noted a significant change among its customers since Bush's February announcement.

"Last summer, about 10% of the machines we were shipping contained the alternative," says Gene Smithhart, Trane marketing manager. "For the first quarter of this year, it was 30-plus %. We expect half of the orders we ship in the

next six months will use HCFC-123. And by next year, we think that will be up to 80 or 90%."

Price is another factor that soon will motivate CFC users to buy alternatives. Currently HCFC-123 and HCFC-141b cost around \$2.00 per lb. When the federal tax of \$1.37 per lb is added to the average CFC cost of about 75 cents per lb, CFCs cost roughly the same as these HCFCs. However, the tax on CFCs is set to almost double next year, making CFCs decidedly more expensive for the first time.

Makers of rigid foam board insulation are poised to eliminate use of CFCs, but most have not yet done so. Facing competition from fiberglass and expanded polystyrene in new construction, manufacturers of rigid polyurethane and polyisocyanurate need a CFC-11 substitute with good insulating properties. (In contrast, flexible-foam manufacturers—who don't need to worry about insulation values—have already largely replaced CFCs with water-blown foams.)

HCFC-141b is turning out to be almost as good an insulator as CFC-11, says Lorraine Aulisio, Celotex Corp.'s vice president for technical services. "The industry has made a commitment to be out of CFCs by the end of 1993, and we likely will make it."

The blowing agent's cost is a significant part of the cost of their products, she says, but HCFC-141b has been found to be more efficient than CFC-11, so not as much is needed. And with CFC taxes going up, HCFC-141b will soon be cheaper anyway.

The fact that toxicity tests on HCFC-141b have not been

Halons: money in the bank

When the Montreal Protocol on Substances That Deplete the Ozone Layer was first negotiated in 1987, halons (fluorocarbons that contain bromine) were considered so essential for fighting fires that their production was subjected only to a freeze, not a mandatory decrease. When the Montreal protocol was strengthened in 1990, they were placed in the same category as CFCs and scheduled to be phased out by 2000—but with exemptions allowed for essential uses. However last year, when a United Nations Environment Program (UNEP)-sponsored study was asked to list what were essential uses of halons and should be exempt from the ban,

the panel decided there was no need to make such a list.

"There is so much halon already that it will last well into the next century if it is carefully banked and conserved," says Stephen O. Andersen, the Environmental Protection Agency director of technology transfer and industry programs, who cochaired UNEP's technical and economics assessment panel. "The solution is not to manufacture more halon but to set up a system for redeployment."

Very little of current halons production is actually discharged to fight fires. Instead, most is stored in tanks in the fire-protection systems of buildings, airplane cockpits, or military

equipment. In the past few years, fire codes have been changed so that discharge testing of the systems now is done with surrogate chemicals rather than halons.

The major hurdles to phasing out halons production are management, not technical challenges, Andersen says. A halons banking system would allow users to withdraw the chemicals when needed as well as to dispose of them in an environmentally sound way by making deposits in the proposed bank. UNEP's halons banking committee is studying the issue and may recommend allowing international trade in recycled halons.

completed is holding back some potential users—and suppliers—of the chemical. So far there are no indications of toxicity problems with HCFC-141b. But industry is being cautious because insulation is used in buildings where people potentially could be exposed to it for decades.

"We're not selling this product into the rigid-foam market until we have the final toxicity data in the [upcoming] fourth quarter," says William Corcoran, Allied-Signal's vice president for public affairs, engineered materials sector. "There's a lot of pent-up demand. The transition won't be slow and gradual but more like instantaneous."

Unlike HCFCs, the second major group of CFC substitutes are not in regulatory limbo. Although they must clear toxicity hurdles, HFCs pose no threat to the ozone layer because they contain no chlorine. However, they are much more expensive, about \$10 per lb.

HFC-134a (CH_2FCF_3) already is being used in a few new automobile air conditioners in place of CFC-12. U.S. car manufacturers plan to gradually phase it into all their models during the next few years.

"When you look under the hood you won't see that much difference," says Gerald Stofflet, General Motor's assistant director of automotive emissions controls. Stofflet is chairman of the Motor Vehicles Manufacturers Association's CFC subcommittee. "But using HFC-134a involves a major redesign, not just [of] the compressor. We had to look at every part of the system. [HFC-134a] operates at higher pressure and needs a new lubricant."

Stofflet sees a looming problem in servicing the air conditioners in older cars and trucks once CFC-12 is no longer available. Car manufacturers have been upgrading the hoses and O-rings in air-conditioning systems since the late 1970s, he says. "There are a lot of cars on the road that all have different materials. We're now looking for new refrigerants and lubricants that would be compatible. If you put 134a and its lubricant into a system designed for CFC-12, you will reduce the durability of the system significantly."

Retrofitting older cars will also require a new desiccant, he says. The industry thinks the cost will be around \$200

per car. For that money car owners will get a system that never cools quite as well as it did when operating with the CFC-12 it was designed for.

HFC-134a also will replace CFC-12 in home refrigerator compressors. It's already in use in a few models in Europe and New Zealand, according to EPA's Andersen. Not all the kinks in the new systems have been worked out yet, however, says AHAM's Samuels.

"We've seen some coking and caking of the compressor with HFC-134a," Samuels says. "It's not a drop-in replacement for CFC-12. There must be a different compressor, new lubricant, and new desiccator. A refrigerator's compressor operates as much in a year as a car's does in a lifetime."

EPA and the Electric Power Research Institute have been sponsoring longer term research aimed at identifying other possible alternatives for CFC and HCFC refrigerants. For example, chemists at Clemson University and the University of Tennessee synthesized a variety of fluorinated propanes, butanes, and ethers that contain neither chlorine nor bromine.

Eleven of the candidates—nine hydrofluoropropanes and two hydrofluoroethers—have been selected by researchers at EPA's Air & Energy Engineering Research Laboratory in Research Triangle Park, N.C., for further evaluation. All these fluorinated compounds have boiling points and critical temperatures that come close to those of fully halogenated CFCs. Computer models indicate the potential substitutes could be more energy efficient than currently used CFC refrigerants.

The Department of Energy's Oak Ridge National Laboratory (ORNL) is comparing the thermodynamic performance of possible refrigerant alternatives in standard refrigerators and heat pumps. "We set up standard operating conditions and run various refrigerants or mixtures of refrigerants through their paces," says Van Baxter, group leader for refrigeration systems at ORNL's building equipment research program.

Baxter's group also is working with the Appliance Re-

search Consortium on the mechanical systems in refrigerators. "We are looking at some of the leading candidates to see if we can optimize the cycle technology," he says.

EPA also is funding research on alternatives to HCFC-22, which is used in home air conditioners and many commercial refrigeration systems and will eventually be phased out. Researchers at the University of Maryland, College Park, have concluded that blends containing HFC-32 (CH_2F_2) are likely candidates.

Both the auto air-conditioning and home appliance industries are about to face new requirements for capturing, reclaiming, and recycling CFCs during servicing. EPA will issue final rules for mobile air-conditioning any day now, whereas regulations for other uses will be proposed later this summer.

Many shops that service auto air conditioners already are trapping and recycling CFC-12, even though the federal regulations are not yet in place. "In the past two years, more than \$1 billion worth of recycling equipment has been sold," says Andersen. The shops that have bought it, he says, are saving time and money, and providing technically better service.

"Some large companies—such as Firestone, Sears, Ford, and GM—made it company policy not to vent CFC-12 in their repair shops," he notes. "Other independent shops converted because their customers asked them. Having your car serviced properly has been the biggest single thing an individual consumer could do in the U.S. to help the environment."

The change to capturing and recycling CFCs from appliances may not go so smoothly. The Clean Air Act states that after July 1 it will be illegal to vent CFCs or HCFCs to the atmosphere during repair, maintenance, or disposal. EPA, however, has not yet published even a draft of the rules enforcing that section of the law.

EPA is expected to require service technicians to be certified and to use registered equipment that meets set stan-

dards. It likely will impose large fines for each instance in which the chemicals are allowed to escape. The agency has worked closely with industry in developing its proposals, so most big companies know more or less what to expect. But that's not necessarily the case for smaller operators.

"Most technicians are independent small businesses," says Samuels. "Many probably don't even know the certification requirement is coming. There's an enormous shortage of recovery equipment."

Trane Co., which sells all sizes and types of air-conditioning equipment, says it and other companies plan to offer training for technicians on a massive scale. "It is no longer business-as-usual in servicing refrigerants, handling refrigerants, or installing refrigerants," says Trane's Smithhart.

"We should have been doing this as an industry for years and years," he says. "In reality this is good business. Not only is it environmentally correct not to blow a charge of CFCs, but it is economically sound. It costs less to do it right than to do it wrong."

One Minneapolis-based company, Appliance Recycling Centers of America (ARCA), already is successfully recovering and reclaiming CFCs from unwanted household appliances. The firm contracts with electrical utilities to pick up old, energy-inefficient appliances from the power companies' customers. ARCA then drains the CFC-12 from refrigerator compressors, cleans it up in its own distillation facility, and sells it.

"Up until about six months ago, there wasn't much enthusiasm for buying recycled and reclaimed CFCs," says ARCA president Jack Cameron. "Now the price has gone up and the supply has gone down. We can't get enough CFC-12 to sell."

ARCA is about to begin recovering CFC-11 from the foam insulation in refrigerators. This fall it will install a system developed by Adelmann of Karlstadt, Germany, that has a certified recovery rate of 99%, Cameron says. In this system, the foam insulation is placed in a chamber under negative pressure where it is shredded and crushed. The pulverizing breaks the bubbles in the foam, releasing CFC-11, which then is removed in a degasification process.

"We feel real good about this," Cameron says. "There's more CFC-11 in the foam than there is CFC-12 in the compressor. And the CFC-11 can be purified without too much trouble."

"There are tremendous business opportunities for people who get going," EPA's Andersen says. "There's a major concern that delay or neglect in moving out of CFCs will lead to shortages in 1995 or 1996. Shortages not just of chemicals, but of capital equipment and trained people to help make the transition."

"Early demand for substitute chemicals and technologies would help companies develop the necessary manufacturing facilities and train technicians and installers. There is time right now to make the transition. There won't be time if you wait too long." □

Some CFC alternatives also face restrictions

Substance	Ozone depletion potential ^a	Major uses	Regulatory outlook
HCFC-22 (CHClF_2)	0.055	Foams, air-conditioning, refrigeration, aerosols	Clean Air Act bans aerosol use after 1993; EPA likely to ban use in new equipment after 2005
HCFC-142b (CH_3CClF_2)	0.065	Foams, refrigeration	EPA likely to ban use in new equipment after 2005
HCFC-141b ($\text{CH}_3\text{CCl}_2\text{F}$)	0.11	Foams, solvents	EPA likely to approve for foam use only and ban use in new equipment after 2005
HCFC-123 (CHCl_2CF_3)	0.02	Foams, air-conditioning, fire fighting	EPA likely to approve only air-conditioning use; Clean Air Act bans use in new equipment after 2015
HFC-134a (CH_2FCF_3)	0	Refrigeration, air-conditioning	No restrictions anticipated
HCFC-124 (CHClFClCF_3)	0.022	Refrigeration, sterilant	Clean Air Act bans use in new equipment after 2015
HFC-125 (CHF_2CF_3)	0	Refrigeration	No restrictions anticipated
HFC-22 (CH_2F_2)	0	Refrigeration, air-conditioning	No restrictions anticipated

^a Estimates from United Nations Environment Program's "Scientific Assessment of Ozone Depletion: 1991." Estimates depend on chlorine content and atmospheric lifetime. Potentials are set relative to CFC-11, which is assigned a value of 1.0.

Pollution Prevention at Chemical Plants Benefits Environment at Low Cost

■ ***New study shows that minimizing generation of waste at source cuts pollution management costs, may boost output***

Lois R. Ember, C&EN Washington

The message of a just-released study is simple and direct: pollution prevention pays. As the New York City-based environmental research organization Inform describes in its study of 27 organic chemical manufacturing plants, preventing the generation of waste at the source achieves environmental and economic benefits with minimal implementation costs. Costs are surprisingly low because simple low-tech strategies are all that are needed for the most part.

Over the past decade stricter environmental regulations, soaring waste management costs, and ever fewer acceptable disposal sites have combined to get the chemical industry to take waste aversion, or source reduction, steps. As this latest study and Inform's 1985 survey of the same chemical plants clearly demonstrate, preventing the generation of waste results in less pollution and therefore less need to manage waste. It also conserves natural resources, makes the workplace safer, and improves product yield and quality. Add all that up and the bottom line is cost savings.

Originally, Inform surveyed 29 plants, but one no longer exists and another no longer manufactures chemicals. The remaining 27 plants in the current study are representative of the organic chemical industry as a whole except in one instance. Because their plants were profiled in Inform's 1985 study, managers at these facilities may be more aware of the potential of source reduction and, therefore, more likely to have implemented

appropriate activities than managers at other U.S. chemical plants.

In the 1985 study, the chemical plants reported only 44 source reduction activities. These typically included changes or refinements to a process, better material handling or equipment maintenance, and/or equipment changes, modifications, or additions. Returning to these same facilities in 1992, Inform documented an additional 137 source reduction initiatives.

Fewer than 15% of the 181 reported source reduction initiatives involved product changes or chemical substitutions (of raw materials producing less waste). However, each time a plant reported a product change, it also reported complete elimination of the targeted waste stream.

"The most exciting finding? Perhaps it's that our research seems to show there is not a limit to source reduction. Even these 27 plants could be making more improvements," says Mark H. Dorfman, assistant director of Inform's chemical hazards prevention program and an author of the new study.

Those 27 facilities reported a total waste reduction of 129 million lb a year, with six reporting reductions of more than 10 million lb a year. In some instances, targeted waste streams have been completely eliminated, and in others reductions of 90% or greater have been achieved. For example, a Ciba-Geigy dye manufacturing plant in Toms River, N.J., eliminated a heavy metals waste stream by shifting the necessary purification steps to an earlier part of the process.

Of course, the reported source reduction programs affected the quantity of hazardous releases reportable under the Toxics Release Inventory. According to Dorfman, "For 1988, without source reduction activities, hazardous releases and transfers at all of the 27 plants surveyed would have been higher by one third."

The cost of achieving waste reduc-

tion is low—in a few cases requiring no capital investment. Moreover, in nearly half the cases, investments of less than \$100,000 were needed. A majority of companies have recouped their initial investments in six months or less.

Dollars saved yearly as a result of source reduction are substantial, amounting to between \$45,000 and \$1 million. Only one source reduction activity reported a net cost increase. This occurred at the Aristech (formerly USS Chemicals) plant in Haverhill, Ohio, which makes such products as phenol, acetone, and α -methylstyrene. When Aristech replaced chromium used for corrosion resistance in its cooling water with a newly available nonmetallic substance, its waste treatment costs increased 40 to 50%.

Even including research and development efforts, the time to implement changes is usually short—generally less than six months. In the case of Ciba-Geigy, for example, two months were needed for the process change.

A majority of the plants surveyed report product yield increases. The reason is simple: Efficiency is usually improved and waste is often reduced dramatically.

Facilities with the most successful pollution prevention programs exhibit at least one of three key features. One is a full cost accounting system that incorporates pollution costs and assigns these expenses to individual processes rather than to general plant overhead. Another is employee training and incentive programs that reach top management and production and maintenance workers. "But perhaps the most surprising outcome of our study," says Dorfman, "is the finding that when leadership comes from operation and environmental managers, those plants have significantly more source reduction activities identified and implemented than those plants in which the leadership is not combined."

What motivates managers to set up pollution prevention programs? Ac-

Preventing waste generation at source pays off for organic chemical plants

Company (location)	Number of source reduction activities	Average reduction (%)	Total amount reduced (thousands of lb per year)	Total saved (\$ thousands per year)	Total capital investment (\$ thousands)	Average payback period (months)	Average yield increase (%)	Implementation time (months)
LARGE PLANTS (> 100 employees)								
Aristech (Ohio)	16	64%(5)	26,929 (6)	\$3755 (6)	\$ 9,492 (7)	16.0 (4)	na	na
Atlantic (N.J.)	9	33 (1)	350 (1)	na	na	na	8.0%(1)	na
Chevron (Calif.)	5	66 (3)	140 (1)	200 (1)	na	na	na	na
Ciba-Geigy (N.J.)	16	76 (11)	293 (6)	1593 (8)	290 (8)	7.2 (8)	12.4 (6)	6.7 (6)
Dow (Calif.)	5	98 (3)	12,160 (1)	2726 (2)	250 (1)	1.3 (1)		5 (2)
Du Pont (N.J.)	13	62 (4)	39,290 (10)	3755 (5)	11,000 (2)	43.6 (1)	0 (1)	3 (1)
Exxon (N.J.)	9	72 (9)	17,089 (6)	3412 (6)	18,700 (3)	47.9 (3)		60 (1)
Fisher (N.J.)	21	43 (8)	629 (15)	529 (5)	79 (5)	8.8 (4)	28.0 (1)	18 (1)
ICI Americas (Calif.)	7	67 (3)	125 (4)	266 (4)				
IFF (N.J.)	11	30 (10)					7.0 (1)	3.5 (2)
Merck (N.J.)	5	50 (1)	12,963 (4)	1048 (2)	1,000 (1)	12.0 (1)		
Monsanto (Ohio)	13	90 (7)	17,330 (5)	3716 (6)	60 (2)	1.2 (2)	8.2 (2)	5.5 (2)
Morton (Ohio)	na	na	na	na	na	na	na	na
PMC (Ohio)	8	85 (6)	91 (3)	260 (2)	25 (1)	na	5.0 (1)	12 (3)
MEDIUM PLANTS (50-100 employees)								
American Cyanamid (Ohio)	6	94 (5)	806 (5)	220 (3)	800 (5)	1.5 (3)	0 (1)	7.1 (6)
Borden (Calif.)	13	95 (13)	293 (6)	47 (6)	39 (5)	11.9 (4)	0 (4)	0.5 (4)
Def-Tec (Ohio)	2	88 (1)	3 (1)	27 (2)	na	na	na	na
Rhône-Poulenc (N.J.)	7	53 (3)	248 (6)	366 (6)	4,260 (5)	11.5 (4)	1.0 (2)	6.5 (4)
Shell (Calif.)	na	na	na	na	na	na	na	na
Unocal (Calif.)	1	100 (1)	na	na	na	na	na	na
SMALL PLANTS (< 50 employees)								
Bonneau Dye (Ohio)	na	na	na	na	na	na	na	na
Colloids (Calif.)	3	na	na	na	na	na	na	na
Hart Chem/ J. E. Halma (N.J.)	na	na	na	na	na	na	na	na
ICI Resins (Calif.)	3	na	na	na	na	na	na	na
Max Marx (N.J.)	0	na	na	na	na	na	na	na
Perstorp (Ohio)	7	72 (4)	na	40 (1)	na	na	na	na
Scher (N.J.)	1	100 (1)	na	na	na	na	na	na

Note: Plants not included: Fibrec (plant no longer exists) and Frank Enterprises (no longer in manufacturing); numbers in parentheses indicate the number of source reduction activities for which data in that category were available: na=not available, no data provided by plants. Source: Inform

cording to the findings of the 1992 study, the problems and costs associated with managing waste is a key motivator, followed closely by environmental regulations. These factors are cited by Frank D. Tejera, plant manager of Borden Chemical's Fremont, Calif., plant, as the reason he got into source reduction. Tejera's facility manufactures adhesives used in making plywood and particle board.

The Borden plant has now "achieved 90 to 95% of the reduction we can. We're still making minor changes, tweaking the system, but the payback is starting to get less attractive," Tejera explains.

Still he waxes enthusiastic about source reduction. "It's been successful beyond our wildest expectation. Source reduction pays. What little investment you make you can get back in spades.

All it takes is a little creativity, doing your homework, and elbow grease."

Massachusetts was the first state to pass a toxic use reduction law, and its Department of Environmental Protection commissioner, Daniel S. Greenbaum, is rhapsodic about the Inform study. "It is extremely valuable to those of us charged with implementing laws mandating the cutting down of wastes. It will help us [regulators] identify factors that make a difference, that get companies to make a change. And it will help us identify obstacles we're putting in front of companies that want to make a change."

In particular, he believes the study will help regulators detect rules that bar innovation or that keep regulators from looking at a whole facility instead of individual sets of pipes. The report,

Greenbaum believes, will also "serve as an independent verification of reductions reported by companies, reports that might otherwise be considered mere boosterism."

Morton L. Mullins, Chemical Manufacturers Association vice president for regulatory affairs, finds the Inform study "balanced, thoughtful—a very useful contribution to the pollution prevention ethic which is clearly evolving in the chemical industry." CMA's Responsible Care guidelines require that member companies institute waste and release reduction programs that emphasize source reduction.

The report, "Environmental Dividends: Cutting More Chemical Wastes," is available from Inform, 381 Park Ave. South, New York, N.Y. 10016, for \$75. □